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# ***U.S. PATENT APPLICATION***

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*Invention:* METHOD FOR TREATING ORGANS SUBJECT TO EROSION BY LIQUIDS AND ANTI-EROSION COATING ALLOY

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## ***SPECIFICATION***

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## METHOD FOR TREATING ORGANS SUBJECT TO EROSION BY LIQUIDS AND ANTI-EROSION COATING ALLOY

The present invention relates to a method for treating organs subject to erosion by liquids and an anti-erosion coating alloy.

In particular, the present invention relates to a method for the coating of organs subject to erosion by liquids, such as vapour turbine components, by means of the laser plating of a cobalt-based alloy.

It is known that the organs of equipment which undergo repeated impact with liquids during functioning, are subject to a slow but continuous erosion destined to jeopardize their functionality and performances after a certain period of operation.

This phenomenon is particularly evident and significant, for example, in vapour turbines whose components are subject to marked wear when specific precautionary measures are not adopted.

Specifically in vapour turbines, the condensation pressure values must be as low as possible in order to obtain the highest outlet power in simple and combined cycles.

Under these operating conditions, the low pressure rotor blades are subjected to different chemical and physical stress and therefore undergo erosion processes due both to the presence of numerous water particles in the vapour flow and also to the high peak rates of the blades.

The erosion phenomena of vapour turbine components, which occur as a result of repeated impact with liquids under prolonged operating conditions, have already been the subject of studies and are documented in Wear, M. Lesser 1995, 28-34.

In order to avoid the drawbacks due to these erosion phenomena, attempts were made to solve the problem, from the design point of view, by increasing the axial spacing between the stator and rotor or by extracting the humidity between the rows of blades through holes or air gaps situated on the blades of the stator.

These remedies did not prove to be particularly suitable for solving the problem, as they cause a reduction in the performances of the turbine.

Attempts were then made to prolong the average operating life of the turbine blades, by studying new coating materials which are capable of reducing the erosion rate of the metals caused by impact liquid separation (F.J. Heymann, ASM Handbook Vol. 18, page 221).

Improvements in this field have so far been reached by resorting to specific treatment on the metal surface of the blades, such as induction or local flame hardening, by means of stellite plate brazing or with tool steels, or by means of hard coatings applied by welding.

In order to evaluate the resistance to erosion, the coating materials of the known art have been subdivided, approximately, into two groups, that of carbides and that of metallic materials among which Stellite 6, according to what is already described in literature for example in the publication "Erosion-resistant Coating for Low-Pressure Steam Turbine Blades, Euromat '99".

Ionic nitriding with PVD coating using titanium nitride and chromium or zirconium nitride were selected for the surface treatment.

The blades subjected to ionic nitriding treatment followed by two subsequent PVD coatings were made up of a layer of titanium nitride followed by a coating of zirconium nitride or chromium nitride.

All the PVD coatings had a thickness of about 3-4  $\mu\text{m}$ . The coating tests showed a coating discontinuity of the models and the behaviour was considered unsatisfactory.

A SEM test revealed that the PVD coating was not substantially capable of opposing impact erosion whereas the nitride layer was subject to lesions as a result of micro-fractures together with the foil nitrides present in the structure.

Blades with metallic coatings were then tested with HVOF (Triballoy 800).

The performances of the Triballoy 800 alloy, as coating material against erosion from liquids, proved to be inadequate.

From the indications obtained in the tests effected, it can in fact be held that these metal alloy coatings are not even as effective, in limiting erosion phenomena, as uncoated surfaces of the base material.

This behaviour on the part of the Triballoy 800 alloy is verified both by the results of the adhesion tests (all the coatings tested did not pass this test) and also through SEM micrographic observation which revealed the presence of numerous micro-fractures in the coating layer. The microstructure of these coatings, in fact, has a high oxide content and a marked porosity which make it unsuitable for resisting erosion by liquids.

Blades with metallic coatings (Stellite 6) were then tested with HVOF.

Although stellite alloys are known as being a material suitable for coating, they show all their limits when applied by means of HVOF. Micrographic analysis, in fact, demonstrates that low content particles are also enveloped in a film of oxide.

This fact is also confirmed by the surface morphology revealed by means of SEM, which shows a detachment or ungluing of the material specifically along these particles.

Blades treated with coatings with HVOF and SD-Gun TM carbides were then tested.

The results obtained with these types of coatings are in some cases comparable to or better than those obtained with the hardened base material (WC-10Co-4CrSD-Gun TM and 88 WC-12Co HVOF).

The cases in which an unsatisfactory behaviour is verified can be explained by the reduced adhesion of the coating and through the known intrinsic fragility (due to the presence of chromium carbides).

Vice versa, the coatings of the known art which provide better results are those made of tungsten carbides with a cobalt or chromium-cobalt matrix, depending on the coating process used.

Coatings which have a good resistance to erosion are characterized by a detachment of the material on a small portion of the sample whereas this phenomenon is extended to a much larger surface of the materials whose resistance properties are considered unsatisfactory.

This different behaviour can be explained by considering the surface morphology.

When the layer of surface coating starts losing its conformation following the loss of material, the liquid/solid interaction is particularly complex. In this situation, the impulse or impact pressures which trigger the erosion phenomenon, are greatly influenced by the point in which there is initial contact with the drops which fall on a crest (slope), developing lower local pressures with respect to the drops which fall into a crater.

In the case of base materials, the low resistance effected by the surface makes the removal of the material almost completely uniform along the whole area involved in the test.

The unsatisfactory behaviour of most of the coatings of the known art can be explained by the reduced adhesion of the coating on the metallic substrate and the well known intrinsic fragility (due to the presence of chromium carbides).

Vice versa, the coatings of the art which provide improved results are those consisting of tungsten carbides with a cobalt, chromium-cobalt matrix, depending on the use of the coating process.

In general, the performances of the coatings with HVOF improve with an increase in the content of tungsten carbide. The micrographic morphology of the 88WC-12Co coating is, in fact, more homogeneous with respect to that of 83WC-17Co. On the other hand, the difference in performance of the same material (WC10Co-4Cr), applied by means of SD-GunTM or HVOF is quite marked. The results of the former are encouraging, whereas those of the latter are unsatisfactory.

This confirms that at present the spraying process has a significant importance in obtaining certain performances of the coating.

The thermal treatment of the known art for increasing the hardness, however, has as yet shown a reduced increase in resistance to erosion due to an excessive fragility.

It has been verified that in the case of coatings by means of thermal spraying, an important parameter for evaluating the resistance to erosion by liquids is the adhesion resistance. A low value immediately suggests that the coating is not appropriate. An additional requisite for resistance to erosion is the good quality of the microstructure of the coating.

At the moment, the necessity is consequently felt for having new types of coating or treatment of organs subject to erosion such as gas turbine components which are capable of effectively reducing the metallic erosion rate due to separation by impact with liquids.

One of the general objectives of the present invention therefore consists in providing an alloy for the coating of organs subject to erosion, such as vapour turbine components, which is highly resistant to metallic erosion phenomena as a result of impact with liquids.

A further objective of the invention consists in providing a method for the treatment of the surfaces of metallic organs subject to erosion by liquid, in particular vapour turbine blades, which effectively increases the adhesion resistance of the coating applied.

The last but not least important objective consists in providing an alloy and a method for the coating of vapour turbine blades which is simple to produce and does not involve high production costs.

It has now been surprisingly found that it is possible to obtain a coating for organs subject to erosion, by applying on the metallic surfaces of said organs a cobalt-based alloy, having a composition which is rich in tungsten and incorporating selected quantities of other elements.

The alloy of the invention is of the stellite or Haynes alloy type, referring to a material which belongs to the group of hard alloys based on cobalt, chromium and tungsten, particularly resistant to corrosion and wear.

In accordance with a first aspect, the applicant has now identified, within the range of cobalt-based alloys, a composition which is particularly suitable for the coating of organs subject to erosion by liquids, such as for example, vapour turbine components, comprising:

chromium from 28 to 32% by weight

tungsten from 5 to 7% by weight

silicon from 0.1 to 2% by weight

carbon from 1.2 to 1.7% by weight

nickel from 0.5 to 3% by weight

iron from 0.01 to 1% by weight;

manganese from 0.01 to 1% by weight;

molybdenum from 0.2 to 1% by weight

cobalt the complement to balance.

The alloy of the invention, conveniently in powder form, can also comprise other optional elements in a quantity ranging from 0 to 0.5% by weight.

The alloy of the invention has a balanced composition of constitutive elements which enhances the properties of anti-erosion by liquid when it is applied to organs subject to erosion according to the method of the invention.

It has been verified that the method and alloy compositions of the invention allow the production of a layer of coating on organs subject to erosion by liquids, which is highly resistant to mechanical stress when functioning, caused by impact with liquid particles.

In particular, from specific tests it has been observed that the use of the alloy of the invention allows the production of coatings having a higher resistance to erosion from impact with liquids by an order of magnitude (for example 2,000,000 of impacts against 180,000 with traditional hardening materials) with respect to the resistance values of other materials used in the known art.

It has also been observed that the application of the composition of the invention to the surfaces of vapour turbine components, such as blades, causes an unexpectedly higher resistance to erosion with respect to the use of stellite alloys of the known type.

The alloy according to the invention advantageously has a selected carbon content to form carbides with a suitable stoichiometry, a chromium and tungsten content selected for obtaining an improved reinforcement for a solid solution and for optimizing the precipitation values of carbides having a suitable stoichiometry. The alloy of the invention advantageously has a selected nickel content to provide a suitable ductility and allow an effective application in the method of the invention.

A selected nickel content which is particularly suitable for optimizing the behaviour of the alloy in laser plating ranges from 0.6 to 2.8% and preferably from 0.9 to 2.5% by weight.

It has been observed that by maintaining the quantities of carbon, chromium, tungsten, nickel and molybdenum within the ranges indicated above, the alloys of the invention have a resistance to erosion by liquids that is higher than the norm.

According to another aspect of the invention, a method is provided for the treatment of an organ subject to erosion by liquids, in particular vapour turbine components, comprising the application of a cobalt-based alloy previously described to the surface of said organ or turbine component, to form a coating layer resistant to erosion by liquid.

According to a preferred embodiment, the method of the invention comprises the application of said cobalt-based alloy by means of laser plating (laser cladding) on organs subject to erosion, such as for example, vapour turbine components.

The method of the invention is particularly suitable for reducing the erosion by liquids of vapour turbine components such as blades, rotor, stator and plates.

The laser plating according to the present invention can typically comprise one or more passages on the surfaces of the metallic organs subject to erosion by liquid, so as to form one or more anti-erosion coating layers.

The method of the invention conveniently comprises the application, on the metallic surface to be treated, of an anti-erosion layer having a thickness ranging from 0.1 to 5 mm, preferably from 0.8 to 3 mm.

According to an embodiment of the invention, the metallic material to be subjected to the treatment of the invention can be previously heated and the alloy of the invention is subsequently applied, conveniently by the use of laser technology.

The laser plating is typically carried out using a CO<sub>2</sub> or Nd-Yag laser apparatus.

According to an embodiment, the method of the present invention combines the laser application technology (laser cladding) with the use of alloys having the formulations described above, thus allowing structures to be obtained, with increased anti-erosion performances due to the high solidification rate and low thermal supply.

It has been verified that the combined use of the alloys of the invention with laser plating gives rise to a) a matrix based on a solid solution over-saturated with the alloy elements, b) an extremely fine grain, c) a precipitation of fine carbines homogeneously dispersed in the matrix, d) an extremely reduced modified thermal area, e) an extremely limited bath dilution.

The differences in the behaviour of a turbine component treated according to the method of the invention and metal components either non-plated or plated with products of the known art are evident from the enclosed drawing in which:

The figure illustrates a graph relating to comparative liquid erosion tests on 4 metal samples.

In particular, the enclosed figure illustrates a graph which indicates in abscissa the number of impacts and in ordinate the volume loss following impact with liquid drops.

The graph summarizes the results of erosion by liquid drops sprayed through a 0.13 mm nozzle on four test samples made of martensite stainless steel, the same material

but with martempering treatment (MT), integral stellite and stainless steel coated with a layer produced by laser plating of the alloy of the invention, according to Example 1.

The graph indicates the increased resistance to erosion by liquid drops of the sample treated according to the invention with respect to the samples of the known art.

Once the coating material, according to the present invention, has been applied to metallic surfaces of vapour turbine components, it has a high adhesion resistance.

The high resistance properties of the coating produced with the method of the invention are also justified by its microstructural morphology.

It has in fact been observed that the structure of the coating produced with the laser technique is extremely fine and the removal of the material, which essentially takes place by means of cracking along the carbide bonds, is reduced even after prolonged periods of turbine activity.

Furthermore, the coating material applied according to the method of the invention only tends to become detached, following prolonged and repeated stress, on a reduced portion of the sample whereas this phenomenon involves a much wider surface area when the coating is made with materials of the known art.

The application of the laser technology consequently makes it possible to produce coatings with a high resistance to erosion by separation due to impact with liquids, reducing alteration of the base material to the minimum. The use of the laser technology also allows stress reducing treatment to be effected at temperatures slightly lower than the recovery temperature, thus avoiding any possible negative effect on the tensile strength.

The following examples are provided for the sole purpose of illustrating the present invention and should in no way be considered as limiting the protection scope according to the enclosed claims.

## EXAMPLE 1

A composition was used, in powder form for the coating of mechanical vapour turbine components having the following formulation:

Cr	30 g
W	6 g
Si	1 g
C	1.5 g
Ni	1.5 g
Fe	<0.3 g
Mn	<0.3 g
Co	48 g
Mo	0.75 g
Other	<0.25 g

The powder was applied to stainless steel turbine blades by means of YAG laser plating (laser cladding) forming an anti-erosion layer having a thickness equal to about 1 mm.

## EXAMPLE 2

The following Table indicates various formulations of compositions in powder form according to the present invention.

Element	Comp. 1	Comp. 2	Comp. 3
Cr	28%	31.5%	30%
W	5.1%	6.5%	6%
Si	0.1%	1.8%	1%
C	1.2%	1.6%	1.5%
Ni	0.5%	2.8%	1.8%
Fe	0.01%	0.9%	0.5%
Mn	0.01%	0.8%	0.3%
Mo	0.2%	0.9%	0.3%
Co	Balance	Balance	Balance
Other	0.01%	0.005%	0.05%